DALTON
COMMUNICATION

Oxidation of gold(I) pyrazolates by aqua regia. X-Ray crystal structures of the first examples of trinuclear Au$^{III}_3$ and Au^{I}Au$^{III}_2$ pyrazolato complexes

Guang Yang and Raphael G. Raptis *

Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, PO Box 23346, San Juan, PR 00931, USA. E-mail: Raphael@adam.uprr.pr

Received 8th August 2002, Accepted 26th September 2002
First published as an Advance Article on the web 7th October 2002

A trinuclear Au$^{III}_3$ pyrazolato complex, prepared by oxidation of (3,5-dimethylpyrazolato)gold(I) with aqua regia, decays sequentially to the mixed-valent Au^{I}Au$^{III}_2$ and Au$^{I}_2$Au^{III} species by elimination of Cl$_2$.

The remarkable resistance of [Au^{I}(μ-3,5-Ph$_2$-pz)]$_3$ to oxidation (pz = pyrazolato anion) was pointed out by Raptis and Fackler several years ago; the triangular nature of the complex is preserved and only a mixed-valent Au$^{I}_2$Au^{III}Cl$_2$ product results, even when such a potent oxidant as aqua regia is employed.[1] Similarly, oxidation of [Au^{I}(μ-3,5-Me$_2$-pz)]$_3$ by I$_2$ has also been reported to yield the corresponding Au$^{I}_2$Au^{III}I$_2$ trinuclear complexes.[2] In contrast to these two pyrazolato complexes, the related trinuclear complex Au$^{I}_3$(μ-LL)$_3$, where LL = benzylimidazolato or MeN=COMe anions, can be sequentially oxidized by halogens to Au$^{I}_2$Au^{III}X$_2$, Au^{I}Au$^{III}_2$X$_4$ and Au$^{III}_3$X$_6$.[3,4]

The introduction of substituents at the 3-, 4-, or 5-position of the pyrazole ring influences its basicity.[5] Investigating the role of peripheral substitution in the context of gold pyrazolate redox chemistry, we report here that the presence of electron releasing methyl substituents at the 3- and 5-pyrazole positions allows the stabilization of the hitherto unknown higher oxidized Au$^{III}_3$ and mixed-valent Au^{I}Au$^{III}_2$ species.

(3,5-Dimethylpyrazolato)gold(I) is an intractable white solid, assumed to be trimeric, [Au(μ-3,5-Me$_2$-pz)]$_3$, by analogy to its known 3,5-R$_2$-pz analogues, R = Ph, CF$_3$[6,7] as well as its Cu^{I} counterpart, [Cu(μ-3,5-Me$_2$-pz)]$_3$.[8] No structurally characterized Au^{I}, Au^{III}, or mixed-valent forms of this complex have been reported to date. Addition of neat, freshly prepared, aqua regia to solid [Au(μ-3,5-Me$_2$-pz)]$_3$, yields an orange-red solid product,† which after dissolution in CH$_2$Cl$_2$ and crystallization is shown by X-ray structural analyses to be a mixture of the trinuclear complexes [Au$^{III}_3$Cl$_6$(μ-4-Cl-3,5-Me$_2$-pz)$_3$] (**1**), [Au^{I}Au$^{III}_2$Cl$_4$(μ-4-Cl-3,5-Me$_2$-pz)$_3$] (**2**) and [Au$^{I}_2$Au^{III}Cl$_2$(μ-4-Cl-3,5-Me$_2$-pz)$_3$] (**3**) (Fig. 1, 2, and 3, respectively). ‡ Along with the oxidation of the Au-centres, the action of aqua regia carries out the chlorination of the 4-position of the pyrazole rings. The composition of the **1**/**2**/**3** mixture is difficult to control and varies with solution concentration and sample age. Methylene chloride solutions of the crude reaction product are initially red coloured, but slowly become paler orange and eventually yellow, as **1** decomposes to **2** and eventually to stable **3** (Scheme 1). Even solid crystalline samples of **1** and **2** decompose to a yellow powder of **3** after less than one month. While aqua regia does not chlorinate the methyl substituents of the pyrazole rings – no chlorination of methyl groups is seen in the crystal structures of **1** and **2** – the partial methyl group chlorination seen in **3** is, evidently, a result of the action of Cl$_2$ liberated by the reductive decomposition of **1** and **2**. The halogenation of methyl groups can result in three mono-, fifteen di- and several higher-chlorinated isomers of **3**. While only two methyl positions are partially chlorinated in the single crystal used for the structure determination of **3** (*vide infra*), the crude reaction product consists of a mixture of several isomers rendering its ^{1}H-NMR spectrum uninterpretable. The photochemical halogenation of alkyls is a well-documented free-radical process.

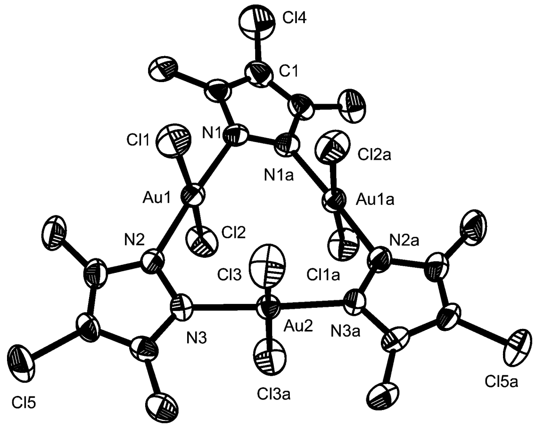


Fig. 1 ORTEP[17] diagram of **1** with atom labeling scheme. A two-fold axis passes through Au2, C1 and Cl4. Selected distances (Å) and angles (°): Au(1)–Au(1a) 3.440(1), Au(1)–Au(2) 3.443(1), Au(1)–N(1) 2.002(8), Au(1)–N(2) 1.990(7), Au(2)–N(3) 2.005(7), Au(1)–Cl(1) 2.268(3), Au(1)–Cl(2) 2.253(3), Au(2)–Cl(3) 2.249(3); N(2)–Au(1)–N(1) 176.2(3), N(3a)–Au(2)–N(3) 176.9(3), Cl(2)–Au(1)–Cl(1) 174.1(1), Cl(3)–Au(2)–Cl(3a) 170.6(2). Symmetry code, a: −*x*, *y*, −*z* + 3/2.

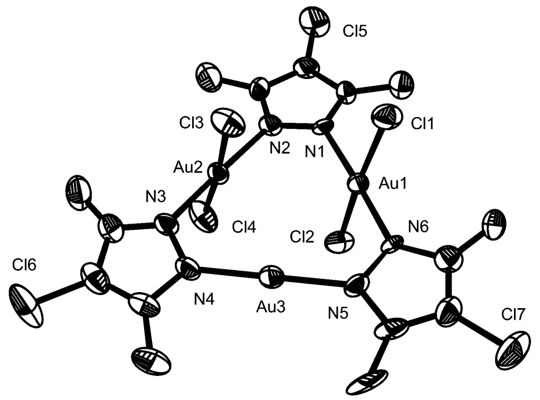


Fig. 2 ORTEP diagram of **2** with atom labeling scheme. Selected distances (Å) and angles (°): Au(1)–Au(2) 3.476(1), Au(1)–Au(3) 3.382(1), Au(2)–Au(3) 3.363(1), Au(1)–N(1) 2.020(10), Au(1)–N(6) 1.985(9), Au(2)–N(2) 2.033(11), Au(2)–N(3) 1.977(11), Au(3)–N(4) 1.991(12), Au(3)–N(5) 1.996(11), Au(1)–Cl(1) 2.276(4), Au(1)–Cl(2) 2.262(4), Au(2)–Cl(3) 2.261(4), Au(2)–Cl(4) 2.266(4); N(6)–Au(1)–N(1) 177.6(5), N(3)–Au(2)–N(2) 178.1(5), N(4)–Au(3)–N(5) 179.1(5), Cl(2)–Au(1)–Cl(1) 174.5(2), Cl(3)–Au(2)–Cl(4) 175.6(2).

The mixed-valent complex [Au^{I}Au$^{III}_2$Cl$_4$(μ-3,5-Me$_2$-pz)$_3$] (**2a**), is prepared in pure form from the reaction of AuCl$_3$py and Na[3,5-Me$_2$-pz] in CH$_2$Cl$_2$.§ Similarly to **2**, complex **2a** gradually decomposes to stable [Au$^{I}_2$Au^{III}Cl$_2$(μ-3,5-Me$_2$-pz)$_3$] (**3a**); monitoring the ^{1}H-NMR spectrum of **2a** over two weeks

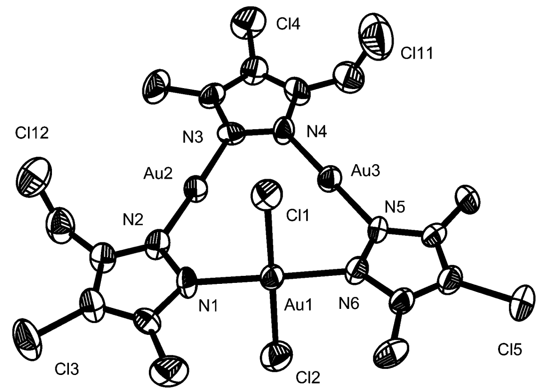
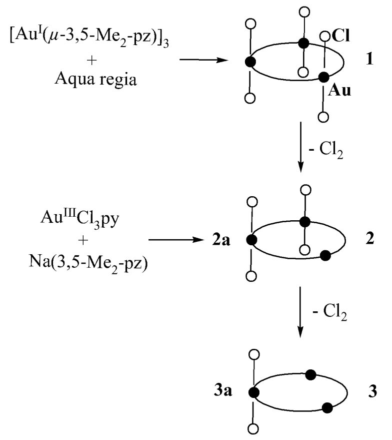
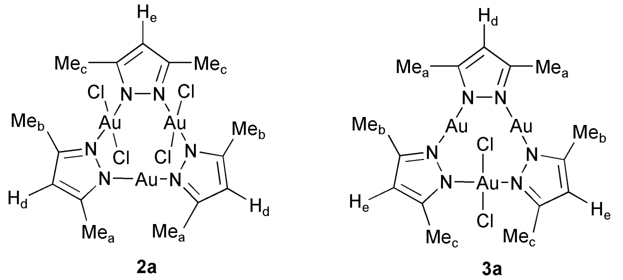


Fig. 3 ORTEP diagram of one of the two crystallographically independent molecules of **3** with atom labeling scheme. The occupancy factors for Cl(11) and Cl(12) are 50% and 20%, respectively. Selected distances (Å) and angles (°): Au(1)–Au(2) 3.414(2), Au(1)–Au(3) 3.398(1), Au(2)–Au(3) 3.333(2), Au(1)–N(1) 1.983(10), Au(1)–N(6) 1.985(11), Au(2)–N(2) 1.982(11), Au(2)–N(3) 1.991(11), Au(3)–N(4) 2.023(11), Au(3)–N(5) 1.994(11), Au(1)–Cl(1) 2.279(4), Au(1)–Cl(2) 2.272(4); N(1)–Au(1)–N(6) 177.6(5), N(2)–Au(2)–N(3) 176.0(5), N(5)–Au(3)–N(4) 179.6(5), Cl(2)–Au(1)–Cl(1) 176.9(2).



Scheme 1



2a **3a**

Scheme 2

shows its gradual decomposition to **3a** (see Scheme 2 for ^{1}H-NMR assignments). The crystallographic and elemental analyses of **2a** and **3a** reveal that they differ from **2** and **3**, respectively, only in that the former have the 4-position of their pyrazole rings only partially chlorinated.¶

The crystal structures of **1**, **2**, **2a**, **3** and **3a** all contain a planar nine-membered $[Au–N–N]_3$ metallacyclic core that remains intact, and approximately three-fold symmetric, over the course of the redox process described here. Small, but statistically significant, differences are seen in the intramolecular Au ··· Au separations showing the trend $Au^{III} \cdots Au^{III} > Au^{III} \cdots Au^{I} > Au^{I} \cdots Au^{I}$. Weak intramolecular Au^I–Au^I aurophilic interactions,[9] or coulombic Au^{III}–Au^{III} repulsions may be responsible for those differences. No chemically significant intermolecular interactions are present in any of the five structures. The Au^I-centres are linear two-coordinate, while the Au^{III} ones are four-coordinate in a slightly distorted square planar *trans*-N_2Cl_2 environment. The N–Au–N angles are in the 176.2(3)–179.6(5)° range. Surprisingly, the expected pattern of longer Au^I–N than Au^{III}–N bonds is not seen here; the Au^I–N distances vary from 1.956(15) to 2.023(11) Å, while those of Au^{III}–N from 1.956(18) to 2.033(11) Å. Backbonding from the Au d^{10} into the pyrazole π* orbitals, as has been previously suggested for $[Au^I(\mu\text{-}3,5\text{-}Ph_2\text{-}pz)]_3$, may be contributing to and shortening the Au^I–N bonds.[10] The Au–Cl bonds are tilted away from the Au_3-triangle centres with values of *trans*-Cl–Au^{III}–Cl angles in the 170.6(2)–176.9(2)° range. The bending of the Cl–Au–Cl angles is more pronounced for the higher oxidized complexes indicating coulombic repulsions among the residual negative charges of Cl-ions.

The characterization of trinuclear complexes **1** and **2** complete the Au^I to Au^{III} series of pyrazolates and open up the area of Au^{III} trinuclear species to further reaction chemistry. The difficulty of oxidizing gold(I) pyrazolates, compared to the analogous trinuclear gold(I) carbeniates and imidazolates, is understandable in view of the better electron donating properties of the latter ligands. Even when the σ-donating ability of pyrazole is enhanced by electron releasing methyl groups at its 3- and 5-positions, the $Au^{III}_3/Au^{III}_2Au^I$ and $Au^{III}_2Au^I/Au^{III}Au^I_2$ redox couples remain more positive than Cl_2/Cl^-, as evident by the spontaneous reductive elimination of Cl_2 from **1** and **2**. In this light, it is not surprising that Minghetti *et al.*'s attempt to oxidize $[Au^I(\mu\text{-}3,5\text{-}Me_2\text{-}pz)]_3$ with excess I_2 only gave a $Au^I_2Au^{III}$ product.[2] On the other hand, with the weakly electron withdrawing phenyl groups as substituents – 3,5-Ph_2-pz – only a $Au^{III}Au^I_2$ complex was isolated from either the reaction of Au^I_3 with aqua regia, or the $AuCl_3py$ reaction with Na(3,5-Ph_2-pz).[1,11] Electronic communication of metal atoms *via* pyrazolato bridges has been reported in a diiridium system, where a mixed-valence species is deactivated towards both oxidation and reduction.[12] The same principle of redox property tuning is extended here to the conjugated $[Au–N–N]_3$ metallacycle. The unusually high $Au^{III/I}$ redox potential of the trinuclear complexes described here are particularly interesting in view of the recent report that a protein of unknown structure containing three gold-atoms, isolated from the gold-sequestering *Macrococcus luteus* bacteria, cycles between Au^I and Au^{III} states as it oxidizes CH_4 to MeOH.[13]

The redox chemistry of the trimeric gold pyrazolates reported here stands in stark contrast to those of other oligomeric gold pyrazolates of different geometries. The reactions of $[Au^I(\mu\text{-}3,5\text{-}{}^tBu_2\text{-}pz)]_4$ and $[Au^I(\mu\text{-}3,5\text{-}Ph_2\text{-}pz)]_6$ with aqua regia, as well as with stoichiometric quantities of Br_2, give predictably the total oxidation product, $[4\text{-}X\text{-}3,5\text{-}R_2\text{-}pzH_2^+][AuX_4^-]$ (X = Cl, Br), as the only product.[14] The extra stability of the +I oxidation state in the planar trinuclear compared to the non-planar tetranuclear (D_{2d}) and hexanuclear (D_2, figure-eight geometry)[15] compounds is tentatively attributed to the ability of the pyrazolate ligands to accept backdonation of electron density into their vacant π* orbitals when they are in a coplanar arrangement. The importance of geometric features, such as the presence or absence of direct metal–metal interactions and the influence of donor or acceptor ligands, in determining the pathway and products of oxidative additions to dimeric and trimeric gold complexes has been discussed by Fackler.[16]

Acknowledgements

G. Y. acknowledges a Lingnan Foundation Fellowship from Zhongshan University. This work is supported by the ARL Collaborative Technology Alliances in Power and Energy, Cooperative Agreement No. DAAD 19-01-2-0010.

Notes and references

† To $[Au^I(\mu\text{-}3,5\text{-}Me_2\text{-}pz)]_3$ (0.1 mmol, 88 mg)[2] 5 ml of freshly prepared aqua regia is added. The white suspension changes immediately to red, the mixture is stirred for 30 min, is filtered through a fritted glass funnel and the red solid is washed with water. Slow solvent evaporation of a CH_2Cl_2 solution of the crude product yields < 5% crystals of **1**, **2** and **3**.

‡ Crystal data (Siemens SMART 1K CCD diffractometer): **1**,

$C_{15}H_{18}Au_3Cl_9N_6$, $M = 1192.30$, orthorhombic *Pbcn*, $a = 14.587(2)$, $b = 13.334(2)$, $c = 14.971(2)$ Å, $V = 2912.0(7)$ Å^3, $Z = 4$, $\mu = 15.921$ mm^{-1}, $T = 298$ K, 5433 reflections collected (1643 unique), 154 parameters, no restraints, $R_1 = 0.0271$ for 1182 reflections with $I > 2\sigma(I)$ (0.0505 for all data), $wR_2 = 0.0476$, $S = 0.950$, max. $\Delta\rho = 0.647$ e Å^{-3}. **2**·CH_2Cl_2, $C_{16}H_{20}Au_3Cl_9N_6$, $M = 1206.33$, monoclinic $P2_1/n$, $a = 7.760(2)$, $b = 29.270(6)$, $c = 13.510(3)$ Å, $\beta = 98.00(3)°$, $V = 3038.7(11)$ Å^3, $Z = 4$, $\mu = 15.258$ mm^{-1}, $T = 298$ K, 14202 reflections collected (4393 unique), 313 parameters, no restraints, $R_1 = 0.0499$ for 3528 reflections with $I > 2\sigma(I)$ (0.0651 for all data), $wR_2 = 0.1258$, $S = 1.120$, max. $\Delta\rho = 1.647$ e Å^{-3}. **3**, $C_{30}H_{33}Au_6Cl_{11.3}N_{12}$, $M = 2144.07$, triclinic $P\bar{1}$, $a = 12.686(3)$, $b = 13.792(3)$, $c = 16.634(3)$ Å, $a = 69.65(3)$, $\beta = 80.95(3)$, $\gamma = 67.60(3)°$, $V = 2521.7(9)$ Å^3, $Z = 2$, $\mu = 18.025$ mm^{-1}, $T = 298$ K, 11123 reflections collected (7247 unique), 559 parameters, no restraints, $R_1 = 0.0399$ for 4672 reflections with $I > 2\sigma(I)$ (0.0747 for all data), $wR_2 = 0.0840$, $S = 0.920$, max. $\Delta\rho = 1.231$ e Å^{-3}.

§ Na(3,5-Me_2-pz) (0.1 mmol, 12 mg) and $AuCl_3py$ (0.1 mmol, 38 mg) are added to 4 ml of dry THF. The resulting solution is stirred for 20 min at 25 °C, the solution color changes from orange-red to yellow, and it is filtered. Hexane is allowed to slowly diffuse into the filtrate, and orange crystals of **2a** appear after standing for 2–3 days (yield: 38%). After a few more days, yellow crystals of **3a** form in 8% yield from the same solution. For **2a**, calculated (for 33% chlorination at the pyrazole 4-position): C, 17.10; H, 1.90; N, 7.98; found: C, 16.67; H, 2.04; N, 7.71%. ^{1}H-NMR (500.13 MHz, $CDCl_3$, ppm) **2a**: 2.43 (s, 6H, Me_a), 2.44 (s, 6H, Me_b), 2.57 (s, 6H, Me_c), 6.24 (s, 2H, H_d), 6.27 (s, 1H, H_e); **3a**: 2.31(s, 6H, Me_a), 2.42 (s, 6H, Me_b), 2.43 (s, 6H, Me_c), 6.20 (s, 1H, H_d), 6.22 (s, 2H, H_e) for the non-chlorinated species and 2.28 (s, 6H, Me_a), 2.42(s, 6H, Me_b), 2.43(s, Me_c), 6.23(s, 2H, H_e) for the species chlorinated at the pyrazole 4-position (H_d replaced by Cl atom).

¶ Crystal data (Siemens SMART 1K CCD diffractometer): **2a**, $C_{15}H_{21}Au_3Cl_4N_6$, $M = 1018.08$, triclinic $P\bar{1}$, $a = 7.625(2)$, $b = 12.505(3)$, $c = 13.495(3)$ Å, $a = 73.88(3)$, $\beta = 86.39(3)$, $\gamma = 85.21(3)°$, $V = 1230.8(4)$ Å^3, $Z = 2$, $\mu = 18.283$ mm^{-1}, $T = 298$ K, 6314 reflections collected (3544 unique), 259 parameters, no restraints, $R_1 = 0.0387$ for 2670 reflections with $I > 2\sigma(I)$ (0.0561 for all data), $wR_2 = 0.0993$, $S = 0.992$, max. $\Delta\rho = 1.397$ e Å^{-3}. **3a**, $C_{15}H_{20}Au_3Cl_{2.22}N_6$, $M = 954.06$, orthorhombic $Pca2_1$, $a = 23.920(5)$, $b = 11.800(2)$, $c = 7.740(2)$ Å, $V = 2184.7(8)$ Å^3, $Z = 4$, $\mu = 20.380$ mm^{-1}, $T = 298$ K, 10747 reflections collected (2898 unique), 250 parameters, 1 restraint, $R_1 = 0.0442$ for 2672 reflections with $I > 2\sigma(I)$ (0.0480 for all data), $wR_2 = 0.1079$, $S = 1.046$, max. $\Delta\rho = 0.713$ e Å^{-3}. CCDC reference numbers 191323–191327. See http://www.rsc.org/suppdata/dt/b2/b207600d/ for crystallographic data in CIF or other electronic format.

1 R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, 1990, **29**, 5003.

2 G. Minghetti, G. Banditelli and F. Bonati, *Inorg. Chem.*, 1979, **18**, 658.

3 (*a*) A. L. Balch and D. J. Doonan, *J. Organomet. Chem.*, 1977, **131**, 137; (*b*) J. C. Vickery and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5978.

4 (*a*) B. Bovio, S. Calogero, F. E. Wagner, A. Burini and B. R. Pietroni, *J. Organomet. Chem.*, 1994, **470**, 275; (*b*) F. Bonati, A. Burini, B. R. Pietroni and B. Bovio, *J. Organomet. Chem.*, 1991, **408**, 271.

5 J. Elguero, G. I. Yranzo, J. Laynez, P. Jiménez, M. Menéndez, J. Catalán, J. L. G. de Paz, F. Anvia and R. W. Taft, *J. Org. Chem.*, 1991, **56**, 3942.

6 H. H. Murray, R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, 1988, **27**, 26.

7 B. Bovio, F. Bonati and G. Banditelli, *Inorg. Chim. Acta*, 1984, **87**, 25.

8 M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson and J. Trotter, *Can. J. Chem*, 1990, **68**, 1444.

9 H. Schmidbaur, *Nature (London)*, 2001, **413**, 31 and references therein.

10 R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem*, 1988, **27**, 4179.

11 R. G. Raptis, H. H. Murray and J. P. Fackler, Jr., *Acta Crystallogr., Sect. C*, 1988, **44**, 970.

12 T. G. Schenk, C. R. C. Milne, J. F. Sawyer and B. Bosnich, *Inorg. Chem.*, 1985, **24**, 2338.

13 L. A. Levchenko, A. P. Sadkov, N. V. Lariontseva, E. M. Koldasheva, A. K. Shilova and A. E. Shilov, *J. Inorg. Biochem.*, 2002, **88**, 251.

14 (*a*) G. Yang and R. G. Raptis, *Inorg. Chim. Acta*, accepted for publication; (*b*) G. Yang and R. G. Raptis, unpublished results.

15 R. G. Raptis, H. H. Murray and J. P. Fackler, Jr., *J. Chem. Soc., Chem. Commun.*, 1987, 737.

16 J. P. Fackler, Jr., *Polyhedron*, 1997, **16**, 1.

17 XP software, SHELXTL-NT Software Reference Manual, version 5.1, Bruker AXS Inc., Madison, WI, 1998.